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铑电极的表面增强拉曼光谱：从可见光到紫外光

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Surface-enhanced Raman Spectroscopy on Rh Electrodes: From Visible to Ultraviolet Region

A Thesis Submitted to the Graduate School in Partial Fulfillment of the Requirements for the Degree of Master of Science

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摘　要

电化学界面中物种的结构和键合是表面科学的主要研究对象之一。拉曼光谱可以从分子水平上获得物种的结构和键合信息，并具有采谱范围宽、适合水溶液体系研究等优点，已成为现场谱学电化学的重要工具之一。但拉曼散射的本质是双光子过程，其量子产率很低。因此当研究对象是表面单层或亚单层分子时，其低灵敏度将成为制约瓶颈。表面增强拉曼散射(SERS)效应能使表面物种的拉曼信号得到几个数量级的放大，从而可以较容易获得高质量的表面物种拉曼光谱。但是仅有粗糙的币族金属以及一些极不常用的碱金属基底具有强 SERS 效应，因此长期以来 SERS 难以应用于在电化学上具有广泛应用背景的过渡金属体系。而且至今 SERS 机理尚未明了。由于存在上述难题，上个世纪八十年代后期有关 SERS 的研究步入低谷。此后，随着仪器灵敏度的提高以及各种 SERS 基底制备方法的发展，使得 SERS 技术在各个方面都取得了重要的进展。例如我们研究组近年来通过优化新一代共焦显微拉曼光谱仪，以及发展一系列纯过渡金属(如 Pt、Fe、Co、Ni 等)的粗糙方法，已经基本克服 SERS 只能用于传统币族金属基底的限制，并证实过渡金属表面存在 1-4 个数量级的表面增强因子。但目前的进展还不足以断言表面拉曼光谱已经成为表面科学中的通用技术。为此，除了在仪器上尽可能地提高检测灵敏度以外，建立和发展制备适合的 SERS 活性表面方法、拓宽可用的激发光波长区间、实现在不同界面下的现场研究都是亟待开展的重要工作。

因此本论文主要以上述三个方面的工作为目标，发展了相关的研究方法：(a) 探索并发展纯金属 Rh 的粗糙方法，以进一步拓宽 SERS 在过渡金属中的研究范围，并将其应用于重要的电化学体系的研究；(b) 将激发光波长从通常使用的可见光或近红外光拓宽到紫外光；(c) 开展固/气界面以及固/液/气三相体系的现场表面拉曼光谱研究。以下分别摘要所获得的主要成果：

一．拓宽 SERS 研究至纯 Rh 电极体系

基于金属 Rh 在催化和电催化领域的重要性，我们探索直接在纯 Rh 电极上获得 SERS 效应的方法。由于制备具有一定粗糙度的表面是获得 SERS 信号的基本前提，我们首先探

索纯 Rh 电极的表面粗糙方法并验证其 SERS 活性，结果如下：

(1) 我们根据前人的一些工作，发展了控电流的方波氧化还原循环法(ORC)，获得了粗糙因子在 10 以内不同粗糙度的 Rh 电极，且其电化学性质和光亮表面的相似。原子力显微镜成像表明该电极表面均匀分布着 100～150 nm 的聚集体，上面叠加 20～30 nm 的小颗粒。以吡啶为模型分子发现其具有较强的 SERS 活性和很好的电化学可逆性与稳定性，其表面增强因子达到三个数量级以上。

(2) 为了研究 Rh 电极上的 SERS 机理，我们首先根据光驱电荷转移(CT)增强机理中吸附分子的 SERS 信号最强的电位受到激光光子能量的调制的特点，利用波长为 514.5 nm、632.8 nm 和 780 nm 的激发光得到吸附吡啶环呼吸振动谱峰强度随电位变化的曲线，发现三者的信号最强的电位比较接近，推断该电极的 SERS 效应中 CT 机理不占主要贡献。为了粗略估计电磁场(EM)增强机理的贡献，我们使用静电场近似理论建立二维阵列椭球模型计算得到的平均增强因子小于实验值。可能是由于该计算方法忽略了椭球之间的偶极耦合，并将实际存在的两种尺度叠加的纳米颗粒简单化为一个理想椭球。我们期待建立更加合理的计算模型。

在上述基础上，我们从和 Rh 电极相关的重要电催化体系以及 SERS 研究中重要吸附分子两个方面开展了以下研究：

(1) 在不同酸度的溶液中，在析氢电位以正，Rh 电极上都存在表面氧化物。它们在氢吸脱附的电位区间在激光的协同作用下可被还原。通过溶剂的氘代实验，我们发现表面氧化物中存在一定比例的氢氧化物。

(2) 研究了随电位变化的饱和吸附 CO 的表面拉曼光谱。在此基础上系统地研究了 Rh 电极上甲醇、甲醛、甲酸等 C_1 分子解离吸附和电氧化行为，发现：在酸性溶液中，甲醇既不发生解离也不被氧化；在中性和碱性三个 C_1 分子体系中，以及酸性的甲醛和甲酸溶液中，C_1 分子在较低电位时总是倾向于解离成吸附的 CO，其覆盖度低于饱和吸附；Rh 电极对这些分子的电催化氧化活性顺序为甲醇<甲醛<甲酸；溶液酸度的降低促进了这些分子的电氧化。

(3) 得到了高质量的吡啶、4,4’-联吡啶、SCN^-等在 SERS 研究中常用的模型分子的表面拉曼光谱。研究了这些强吸附物种在不同电位区间的吸附行为。结合 SERS 表面选律，发现吡啶和 4,4’-联吡啶在表面上可能都是以垂直或略倾斜的取向吸附。SCN^-通过硫端吸附

在表面；电位调制过程中，可能由于吸附氧的移去或生成，使得吸附分子所处的微环境发生变化，导致 C≡N 振动的半峰宽发生明显的变化。

二．使用紫外激光为激发线的 SERS 研究

无论从实际应用中获得大分子的表面共振增强拉曼光谱的角度，还是从理论上有关 EM 和 CT 机理研究的角度上看，利用紫外激发的 SERS 研究都具有重大的意义。尽管二十多年来有许多研究者尝试这方面的工作，但至今还没有相关的报道。我们使用了共焦显微拉曼光谱仪和新发展的粗糙金属 Rh 基底方法，首次以波长为 325 nm 的激发光获得了紫外区表面增强拉曼散射（UV-SERS）信号。该部分是本论文工作的最重要成果，具体体现在以下三个方面：

(1) 获得 Rh 电极上吸附吡啶的 UV-SERS 信号，发现 SERS 信号随电位负移增强的同时伴随着较强的光解现象，直至光解产物的信号掩盖了吸附吡啶的信号。酸性溶液中吸附苄氰也可以在较正的电位观察到 UV-SERS 信号，但负电位区也存在强烈光解。类似的现象也发生在一些具有芳环分子的体系。

(2) 为了寻找相对稳定的体系，我们开展了 Rh 电极上较稳定的小分子 SCN^-、CO 的 UV-SERS 研究，得到了较稳定和较高质量的 UV-SERS 谱图。两个体系的表面增强因子都在两个数量级以上。和可见光激发相比，紫外光激发下线性吸附 CO 的 C≡O 振动频率有明显的蓝移，且无法观察到桥式吸附 CO，这可能是由于紫外光诱导桥式吸附 CO 向线性吸附转变。

(3) 通过对 Rh 和 Ag 的介电常数的分析，发现在紫外光区金属 Rh 比 Ag 可能有更大的表面等离子体增强。为此，我们建立阵列椭球模型，采用静电场近似对不同长径比的金属纳米粒子在紫外光区的表面增强因子进行计算，发现若采用波长为 325 nm 激发线，Rh 椭球纳米粒子可能存在两个数量级的增强，而 Ag 几乎没有增强。

三．过渡金属固/气界面以及固/液/气三相体系的现场拉曼光谱研究

电化学固/液界面中物种的行为受很多因素的影响，而作为异相催化领域主要研究对象的固/气界面体系则相对简单。研究固/气界面物种的行为有助于我们更好地理解在固/液界面的相同物种的行为。因此在发展了具有稳定的 SERS 活性的 Pt 族金属基底之后，我们开展了固/气界面上的表面拉曼光谱研究，结果如下：

(1) 新鲜的 Rh 表面在常温下在空气中就可以生成氧化物。Rh 的表面氧化物在惰性气氛中要在 400 ^{o}C 左右的温度下才能分解，而在 H_2 气氛中在 150 ^{o}C 左右就可以完全被还原。无氧化物的 Rh 表面在干燥 O_2 中在室温下也可以生产表面氧化物。

(2) 在固/气界面下，我们得到谱图质量较好的纯金属Rh表面吸附CO的拉曼光谱:在室温,下吸附CO和少量表面氧化物共存;温度上升表面氧化完全消失; 150 ^{o}C以上,吸附的CO开始分解，导致CO覆盖度逐渐降低。将饱和吸附CO的Rh表面置于Ar气氛中,表现出相对较低C≡O振动频率，表明CO吸脱附是一个动态过程。这种现象在Pt体系中更加明显。

(3) 利用H_2和吡啶蒸汽的混合气，我们得到质量较好的Rh表面吸附Py的表面拉曼光谱，吡啶可能以垂直或略倾斜的方式吸附，并可能存在两种不同类型的吸附吡啶。

为了更方便同时进行两种界面的研究，而且使同一物种在固/液和固/气体系的结果可以更好的进行比较，并在固/液和固/气二种界面之间建立起桥梁，我们建立了适合表面拉曼光谱研究的三相体系：

(1)我们提出具有固/液/气三相体系的表面拉曼光谱研究模型,设计加工了可变温、变压、更换溶液的三相电解池，并成功将之应用于变温和流动体系的研究。研究表明固/液体系温度的上升促进了 Pt 电极上 CH_3OH 的解离、氧化以及 CO 的氧化等反应。

(2) 利用上述电解池我们进行了粗糙 Pt 电极/酸性甲醇溶液/空气三相体系的初步研究。在固/液界面，通过控制电位由甲醇解离产生单层吸附的 CO，在不含 CO 的固/气界面检测到了吸附 CO 的拉曼信号。我们认为 CO 可能从较高覆盖度的固/液界面经过表面扩散到达低覆盖的固/气界面。首次证实可以利用拉曼光谱直接观测吸附物种在固体表面的扩散。

总之，我们首先发展了纯 Rh 电极的表面粗糙法(即控电流的方波交流电 ORC 法)，证实了在纯 Rh 上具有 SERS 效应，成功将之应用于相关的吸附和电催化体系的研究。然后在 SERS 研究方法上实现了两个方面的拓宽：即将激发光波长从可见光拓宽到紫外光，将研究对象从纯电化学界面拓宽到了固/气界面以及固/液/气三相体系。由于硕士论文时间的限制，有些结果仍是比较初步的，但是其结果展示了表面拉曼光谱正在发展成为适用性广、研究能力强的表面科学和谱学电化学技术，同时也加深了我们对 SERS 机理的理解。

Surface-enhanced Raman Spectroscopy on Rh electrodes: From Visible to Ultraviolet Region

Abstract

To study the structure and bonding of species in electrochemical interfaces is one of the most important tasks for surface science. Raman spectroscopy, with its particular advantages of wide spectral range and being suitable for the investigation in aqueous solutions and the ability to obtain the structural and bonding information of species at the molecular level, has developed to be one of the important tools in the in-situ spectroelectrochemistry. However, as Raman scattering is intrinsically a double-photon process and has very low quantum efficiency，the poor sensitivity becomes a fatal disadvantage when the surface species investigated is only at an amount of one or even sub- monolayer. The fact that surface-enhanced Raman scattering (SERS) effect can enhance the Raman signal of surface species by several orders of magnitude, makes the good quality Raman spectra easily achievable. Unfortunately, this eminent enhancement only exists on some specially prepared substrates of coinage metals and some scarcely used alkaline metals. This has hindered for a long time the application of SERS in the field of transition metals that are of much wider application in electrochemistry. Moreover, the SERS mechanism is still not well understood up to date. Due to these problems, the SERS study had been shrinking in the late 1980s. Great advances have been made in every aspect of SERS with the rapid improvement of the detention sensitivity of Raman spectrometer and the development of various methods for preparing SERS substrates. As far as our group is concerned, we have circumvented essentially the obstacle that the SERS can only be used on coinage metals and demonstrated the existence of 1-4 orders of magnitude by optimizing the detection sensitivity of the confocal Raman microscope and developing various methods for preparing SERS-active substrates (such as Pt, Fe, Co, Ni, etc.). In spite of current advances, it is still not the time to conclude that surface Raman spectroscopy has been developed into a general technique in surface science. Therefore, besides a further improvement of the detection sensitivity of Raman

spectrometer, it is also important to develop methods for preparing various types of SERS substrates, to extend excitation wavelength to a full range from IR to UV region, and to perform in-situ investigation in different interfaces.

The present thesis is aimed at the above mentioned three fields, and have developed relevant methodologies: (a) explored and found an appropriate roughening method for Rh which extends the further application of SERS to transition metal surfaces and performed the related SERS study of the some important electrochemical systems; (b) performed SERS study excited with ultraviolet (UV) laser other than the conventionally used visible or near-IR laser; and (c) performed surface Raman spectroscopic study of the solid/ gas interfaces and solid/ liquid/ gas three-phase systems. Main results achieved are given below.

1. Extending SERS study to massive Rh electrodes

Due to the important role of Rh in catalysis and electrocatalysis, we tried to obtain a massive Rh electrode of SERS activity. The prerequisite for obtaining SERS signal is the necessity of a certain roughness on the surface. Therefore, as the first task of present thesis was to explore a method to roughen the Rh electrode and create SERS activity. The main results are given as follows.

1) Benefited from previous investigations of other groups, we developed a method, which is to use square wave oxidation-reduction cycles (ORCs) with controlled current, to roughen the Rh electrode, and produced roughened Rh electrodes with the surface roughness factor lower than 10. The electrochemical properties of the electrodes are similar to the smooth one. The surface is composed of uniformly distributed aggregates in the dimension of 100-150 nm with small particles of 20-30 nm on each aggregates as seen from the atomic force microscope images. The electrode shows rather good SERS activity, good reversibility during the potential tuning, and good stability. The surface enhancement factor of adsorbed pyridine on the electrode was estimated to be higher than 3 orders of magnitude.

2) For the purpose of understanding the SERS mechanism of the roughened Rh electrode, different excitation lines (514.5 nm, 632.8 nm and 780 nm) were used to obtained the intensity-potential profiles for the ring breath vibration mode of the adsorbed pyridine. This

experiment was done based on the feature of the photon-driven charge transfer (CT) mechanism, i.e. the potential where the SERS signal of an adsorbed molecule reaches the maximum value depends on the energy of the incident photon. However, we did not find observable shift in the peak potential for the three excitation lines indicating negligible contribution of the CT mechanism. In order to roughly estimate the contribution of electromagnetic (EM) enhancement, we built up a 2D spheroid array model according to the theory of electrostatic approximation. The average enhancement by calculation is smaller than is experiment. The possible reason for this deviation may arise from the neglect of the dipole coupling between the spheroids and the simplification of the real nanoparticles consisting of two different dimension particles as an ideal spheroid.

Based on the aforementioned results, we carried out investigations on the following two aspects: SERS investigation of electrocatalytic relevant systems and the adsorption of some important model molecules.

1) The surface oxides was found to exist on the Rh electrode in solutions with different acidities when the potential is more positive than that for the occurrence of hydrogen evolution reaction. With the synergetic effect of laser, the oxides can be reduced in the potential region of hydrogen adsorption. The experiment using deuterated water demonstrates the existence of hydroxides in the surface oxides.

2) Potential dependent surface Raman spectra of the saturated adsorbed CO on Rh have been obtained. This success allows for a systematic studies on the adsorption and electrooxidation of C_1 molecules such as methanol, formaldehyde and formic acid, etc.. Except that no observable reaction has been observed for methanol in acidic solutions, these molecules tend to dissociate into adsorbed CO, with coverages lower than the saturated adsorption, in the negative potential region in acidic, neutral and basic solutions. The electrocatalytic activity of the Rh electrode to these molecules increase by the order CH_3OH< HCHO< HCOOH in the acidic solutions. The decrease in the acidity of the solutions increases the electrooxidation efficiency.

3) Further studies were with potential dependent behavior of strongly adsorbed pyridine, 4,4’-bipyridine and SCN^-, important model molecules to SERS. The orientation of adsorbed

pyridine and 4,4'-bipyridine are determined both to be perpendicular or slightly tilted to the surface using the surface selection rule. SCN^- is adsorbed to the substrate with the S atom. During the potential tuning, the local environment of the adsorption molecule changes possibly due to the removal and formation of adsorbed oxygen, leading to the remarkable change in the full width of half maximum (FWHM) of the CN vibration.

2. SERS studies with a UV laser as the excitation line.

It is of great significance to perform SERS studies with UV excitation line no matter from the point of view of obtaining the surface-enhanced resonance Raman spectra of large molecules in the practical application, or studying the EM and CT mechanisms theoretically. Despite of great effort made in the past two decades, there is no report up to now in this field. For the first time, we obtained the SERS signal with UV excitation (UV-SERS) using the 325 nm line from a He-Cd laser. The success is attributed partly to the use of a confocal Raman microscope and majorly to the newly developed roughening method for Rh electrode. This work is the most significant achievement of this thesis. Details are given as follows:

1) The UV-SERS signal of the adsorbed pyridine on a Rh electrode has been obtained and becomes stronger with the negative movement of the electrode potential accompanying by an increasing photochemical decomposition till it is totally submerged by the products of photo-decomposition. The UV-SERS signal of adsorbed benzonitrile can only be obtained in the positive potential region in the acidic solution, and photo-decomposition also occurs in the negative potential region. Similar phenomena have also been observed in some aromatic molecule systems.

2) SER spectra with good quality and stability have been obtained for SCN^- and CO, which are relatively stable on the Rh surface against the UV laser illumination. The surface enhancement factors of these two systems were calculated to be over 2 orders of magnitude. The $C\equiv O$ frequency of the on-top adsorbed CO with UV excitation has an obvious blue-shift and no signal related to the bridge-bond CO has been detected, which is remarkably different from the result obtained with visible excitation. It may be due to the transition of bridge-bond CO to on-top adsorbed CO induced by the UV laser.

3) A qualitative analysis of the dielectric constants of Rh and Ag reveals that Rh may have a higher surface plasmon enhancement than Ag. In order to have a quantitative result, we constructed a model of 2D spheroid array based on the electrostatic approximation to calculate the enhancement for metallic nanoparticles of different aspect ratio. The results show that the enhancement of Rh is about 2 orders of magnitude, while that of Ag is nearly zero with the excitation line around 325nm.

3. In-Situ Raman spectroscopic studies of solid/ liquid interfaces and solid/ liquid/ gas three-phase systems of transition metals.

The behavior of species in the solid/ liquid interfaces is influenced by many factors, while that in the solid/ gas interfaces, a major subject of heterogeneous catalysis, is relatively simple. The detailed information from solid/gas interfaces may help a better understanding of the behavior of the same species in the solid/ liquid interfaces. Therefore, a preliminary surface Raman study of solid/ gas interfaces was performed on stable SERS-active Pt-group metal substrates. Main results are given below.

1) The Raman feature of surface oxides was observed on the freshly prepared Rh surface when exposed in air at room temperature. The decomposition of the surface oxides does not occur in the inert atmosphere at until about 400 ^{o}C, while they can be completely reduced by H_2 at about 150 ^{o}C. The oxidation of the oxide-free Rh surface occurs at room temperature in the dry O_2 atmosphere.

2) The surface Raman spectra of the adsorbed CO on Rh in the solid/ gas interface have been obtained. At room temperature, the adsorbed CO coexists with a small amount of surface oxides; with the increase of the temperature, the surface oxides disappear completely; at the temperature higher than 150 ^{o}C, the decomposition of adsorbed CO occurs leading to the decrease of the CO coverage. Leaving the Rh surface with saturatedly adsorbed CO in Ar leads to a lower C≡O vibration frequency, indicating that CO adsorption is a dynamic process. Similar phenomenon occurs in the Pt system more obviously.

3) We have also obtained the surface Raman spectra with good quality of the adsorbed pyridine on Rh in the mixture of H_2 and pyridine vapor. Pyridine may stand perpendicular or slightly

tilted to the surface, and there might exist two kinds of adsorbed pyridine.

In order to make a better comparison of the results obtained from solid/ liquid and solid/ gas interfaces and to bridge the gap between the two interfaces, we built up a three-phase system that is suitable for studying using Raman spectroscopy.

1) We proposed a model that is suitable for investigating the three-phase system using Raman spectroscopy, designed and fabricated a three-phase cell capable of changing the temperature, pressure and the solution and have successfully employed it to investigate the temperature-controlled and flowing solution systems. It was found that the dissociation and oxidation of methanol and the oxidation of CO can be enhanced with the increasing temperature.

2) Based on this cell, we performed the study on the roughened Pt electrode/ acidic methanol solution/ air three-phase system. In the solid/liquid interface, the adsorbed CO was generated from the dissociation of methanol by controlling the potential. The Raman signal of CO was detected in the solid/ gas interface which is in absence of CO. The possible reason could be the surface diffusion of CO from the solid/ liquid interface of higher coverage to the solid/ gas one of lower coverage. Therefore, we demonstrate for the first time that Raman spectroscopy can be used to monitor the surface diffusion of adsorbed species.

In summary, we developed a roughening method for obtaining SERS-active massive Rh electrodes using the square wave ORCs with controlled current, and confirmed the existence of SERS on pure Rh. We further applied it successfully to the studies of the adsorption and electrocatalytic systems of interested. Based on this, we made two further extensions on the SERS methodologies, one being the extension of the excitation line from visible to UV region, the other being the extension of SERS study from pure electrochemical interfaces to the solid/ gas interfaces and the solid/ liquid/ gas three-phase systems. Apparently, some of the results are still preliminary due to the time limitation for a M. Sc thesis, however, the above study show that surface Raman spectroscopy is becoming a general and powerful tool for spectroelectrochemistry and surface science, and have deepened our understanding of the SERS mechanism.

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第一章： 绪论

§1-1 固体表面概述

1-1-1 固/液和固/气界面

两个不同相的接触，必然存在着中间过渡区域。表面是指固体向真空过渡的区域，通常定义为固体最外 3-5 个原子层。当固体与周围环境，例如外部的固、液、气以及电磁辐射相互作用时，很大程度上是在固体的表面上进行的，只有与 X 射线、宇宙射线或者核辐射等作用时才可能和固体体相有关。固体是传统的物质三态之一，人们认为等离子体是物质的第四种形态。而表面也可以认为是物质的一种形态[1]，不论它是金属或半导体表面，还是离子或共价固体表面。它们和物质的其它形态，如固相、液相、气相、溶液、等离子体等，既有相似也有不同。不同之处是其具有自己的结构和化学特性，相似之处是它们都具有相同的微观规律、相同的第一性原理和相似的研究方法。这些相似之处将表面和其它相的科学联系起来，而这些差异使表面具有独特的科学和经济价值。两个相的中间过渡区称为界面(interface)，为了区别于上述各种物质形态，人们将之称为界面相(interphase)。不论我们是否意识到，界面相是极为广泛存在的物质形态，并且在自然界中有着不可替代的作用。例如电化学或其它异相催化的主要步骤就是在这样的场所进行的。以表面或界面为研究对象的学科称为表面科学。

电化学也许是表面科学中最重要的分支，而固/液界面(在电化学中也称为电极/电解质界面)是电化学中最重要的研究对象。因为电化学体系的化学过程，特别是电子传递过程，是在这个界面发生的。它的表面结构、表面上的物种以及这些物种同表面的相互作用情况，决定了这个界面的性质以及可能发生的物理化学过程。固/液界面可以分为三个层面[2]：一是固体表面的原子结构或电子态形貌；二是固体表面吸附层的性质；三是和固体表面相邻的液层。我们可以用图 1-1 所示的模型来理解这样的界面[3]。首先，表面上带电和具有偶极性的物种决定了该界面的电场或电位分布。由于这个电场可以高达 $10^9 V*cm^{-1}$，因此它的存在和分布情况对界面反应的活化能有很大影响。同一电极表面上同一电极反应的速率随着电极电位的改变有很大变化，甚至达到 10 个数量级以上。同样的电极电位，在改变电位分布的情况下也会影响电极的反应速度。这些是电极/电解质界面的电场因素。另一